Thermodynamics of materials

20. Chemical potentials of Atomic Defects III

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Table of Contents

Table of Contents

Chemical Potential of Schottky Defects

- The creation of a Schottky defect can be expressed as

$$\mathsf{A}_{\mathsf{A}}^{\mathsf{AB}} + \mathsf{B}_{\mathsf{B}}^{\mathsf{AB}} \leftrightarrow V_{\mathsf{A}}^{\mathsf{AB}} + V_{\mathsf{B}}^{\mathsf{AB}} + \mathsf{AB}$$

where $\mathsf{A}_{\mathsf{A}}^{\mathsf{AB}}$ represents an A atom occupying on the A sublattice of compound AB, and other notations are used in consistent ways.

- At equilibrium,

$$\mu_{\mathsf{A}}^{\mathsf{AB}} + \mu_{\mathsf{B}}^{\mathsf{AB}} = \mu_{V_{\mathsf{A}}^{\mathsf{AB}}} + \mu_{V_{\mathsf{B}}^{\mathsf{AB}}} + \mu_{\mathsf{AB}}^{\circ}$$

- In the dilute solution approximation,

$$\mu_{\mathsf{A}}^{\mathsf{AB}} = \mu_{\mathsf{A}}^{\mathsf{AB},\circ} + k_{\mathsf{B}} T \ln \left(\frac{N_{\mathsf{A}} - n_{V_{\mathsf{A}}}^{\mathsf{AB}}}{N_{\mathsf{A}}} \right)$$

$$\mu_{\mathsf{B}}^{\mathsf{AB}} = \mu_{\mathsf{B}}^{\mathsf{AB},\circ} + k_{\mathsf{B}} T \ln \left(\frac{N_{\mathsf{B}} - n_{V_{\mathsf{B}}}^{\mathsf{AB}}}{N_{\mathsf{B}}} \right)$$

$$\mu_{V_{\mathsf{A}}^{\mathsf{AB}}} = \mu_{V_{\mathsf{A}}^{\mathsf{AB}}}^{\circ} + k_{\mathsf{B}} T \ln \left(\frac{n_{V_{\mathsf{A}}}^{\mathsf{AB}}}{N_{\mathsf{A}}} \right) = \mu_{V_{\mathsf{A}}^{\mathsf{AB}}}^{\circ} + k_{\mathsf{B}} T \ln \left(x_{V_{\mathsf{A}}^{\mathsf{AB}}} \right)$$

$$\mu_{V_{\mathsf{B}}^{\mathsf{AB}}} = \mu_{V_{\mathsf{B}}^{\mathsf{AB}}}^{\circ} + k_{\mathsf{B}} T \ln \left(\frac{n_{V_{\mathsf{B}}}^{\mathsf{AB}}}{N_{\mathsf{B}}} \right) = \mu_{V_{\mathsf{B}}^{\mathsf{AB}}}^{\circ} + k_{\mathsf{B}} T \ln \left(x_{V_{\mathsf{B}}^{\mathsf{AB}}} \right)$$

Chemical Potential of Schottky Defects

- Since the chemical potential of a compound is the sum of the chemical potentials for each component, i.e.,

$$\mu_{\mathsf{A}}^{\mathsf{AB},\circ} + \mu_{\mathsf{B}}^{\mathsf{AB},\circ} = \mu_{\mathsf{AB}}^{\circ}$$

we have

$$x_{V_{\mathsf{A}}^{\mathsf{AB}}} x_{V_{\mathsf{B}}^{\mathsf{AB}}} = \exp\left[-\frac{\mu_{V_{\mathsf{A}}^{\mathsf{AB}}}^{\circ} + \mu_{V_{\mathsf{B}}^{\mathsf{AB}}}^{\circ}}{k_{\mathsf{B}}T}\right] = \exp\left[-\frac{\mu_{\mathsf{S}}^{\circ}}{k_{\mathsf{B}}T}\right]$$

where μ_{S}° is the chemical potential of a Schottky defect.

Chemical Potential of Schottky Defects

- If

$$x_{V_{\mathsf{A}}^{\mathsf{AB}}} = x_{V_{\mathsf{B}}^{\mathsf{AB}}}$$

then

$$x_{V_{\mathsf{A}}^{\mathsf{AB}}} = x_{V_{\mathsf{B}}^{\mathsf{AB}}} = \exp\left[-\frac{\mu_{\mathsf{S}}^{\circ}}{2k_{\mathsf{B}}T}\right]$$

- In Schottky notation using building elements,

$$0 \leftrightarrow (V_{\mathsf{A}}^{\mathsf{AB}} - \mathsf{A}_{\mathsf{A}}^{\mathsf{AB}}) + (V_{\mathsf{B}}^{\mathsf{AB}} - \mathsf{B}_{\mathsf{B}}^{\mathsf{AB}}) + (\mathsf{AB})_{\mathsf{res}}$$

where $(\mathsf{AB})_{\mathsf{res}}$ represents a molecule of AB compound from a chemical reservoir of compound AB.

Chemical Potentials of Neutral Dopants

- The chemical potential of neutral dopants, μ_{d}° is

$$\mu_{\mathsf{d}^{\times}} = \mu_{\mathsf{d}}^{\circ} + \Delta\mu_{\mathsf{d}}^{\circ} + k_{\mathsf{B}} T \ln\left(\frac{N_{\mathsf{d}^{\times}}}{N_{\mathsf{L}}}\right)$$

  where μ_{d}° is chemical potential of pure dopant d at temperature T and ambient pressure, and N_{L} is the total number of host lattice sites.

- The formation energy $\Delta\mu_{\mathsf{d}}^{\circ}$ of dopant d in a host includes the formation energy and it does not include configurational entropy configuration. With quantity

$$x_{\mathsf{d}^{\times}} = \frac{N_{\mathsf{d}^{\times}}}{N_{\mathsf{L}}}$$

  we have

$$\mu_{\mathsf{d}^{\times}} - \mu_{\mathsf{d}}^{\circ} = \Delta\mu_{\mathsf{d}}^{\circ} + k_{\mathsf{B}} T \ln x_{\mathsf{d}^{\times}}$$

Chemical Potentials of Neutral Dopants

- The solubility limit $x^{\circ}_{\mathsf{d}^{\times}}$ of d in host is given by

$$0 = \Delta\mu^{\circ}_{\mathsf{d}} + k_{\mathsf{B}} T \ln x^{\circ}_{\mathsf{d}^{\times}}$$

Chemical Potentials of Holes and Electrons

- For n-type semiconductor, N_c is the effective electron density of states at the conduction band edge and N_d is the number of electron donors per unit volume.
- For p-type semiconductor, N_v is the effective hole density of states at the valence band edge and N_a is the number of electron acceptors per unit volume.
- The chemical potentials of electrons and holes without electric field is

$$\mu_\mathsf{e} = E_\mathsf{c} + k_\mathsf{B} T \ln\left(\frac{n}{N_\mathsf{c}}\right) \simeq E_\mathsf{c} + k_\mathsf{B} T \ln\left(\frac{N_\mathsf{d}}{N_\mathsf{c}}\right)$$

$$\mu_\mathsf{h} = -E_\mathsf{v} + k_\mathsf{B} T \ln\left(\frac{p}{N_\mathsf{v}}\right) \simeq -E_\mathsf{v} + k_\mathsf{B} T \ln\left(\frac{N_\mathsf{a}}{N_\mathsf{v}}\right)$$

Chemical Potentials of Holes and Electrons

- For $p - n$ junctions, the electric field presents at the junction region, the electric field at n-type semiconductor ϕ^n and the field in p-type semiconductor is ϕ^p,

$$\tilde{\mu}_{\mathsf{e}} = E_{\mathsf{c}} - e\phi^n + k_{\mathsf{B}} T \ln\left(\frac{N_{\mathsf{d}}}{N_{\mathsf{c}}}\right)$$

and

$$\tilde{\mu}_{\mathsf{h}} = -E_{\mathsf{v}} + e\phi^p + k_{\mathsf{B}} T \ln\left(\frac{N_{\mathsf{a}}}{N_{\mathsf{v}}}\right)$$

Chemical Potentials of Holes and Electrons

- At equilibrium,

$$0 = \tilde{\mu}_{\mathsf{e}} + \tilde{\mu}_{\mathsf{h}}$$

therefore,

$$0 = E_{\mathsf{c}} - e\phi^n + k_{\mathsf{B}}T \ln\left(\frac{N_{\mathsf{d}}}{N_{\mathsf{c}}}\right) - E_{\mathsf{v}} + e\phi^p + k_{\mathsf{B}}T \ln\left(\frac{N_{\mathsf{a}}}{N_{\mathsf{v}}}\right)$$

proceed to

$$\Delta\phi = \phi^n - \phi^p = \frac{E_{\mathsf{g}}}{e} + \frac{k_{\mathsf{B}}T}{e} \ln\left(\frac{N_{\mathsf{d}}N_{\mathsf{a}}}{N_{\mathsf{c}}N_{\mathsf{v}}}\right) = \frac{k_{\mathsf{B}}T}{e} \ln\left(\frac{N_{\mathsf{d}}N_{\mathsf{a}}}{n_i^2}\right)$$

where

$$E_{\mathsf{g}} = E_{\mathsf{c}} - E_{\mathsf{v}}$$

the band gap energy and n_i is the intrinsic concentration of electrons and holes without dopants,

$$n_i^2 = N_{\mathsf{c}}N_{\mathsf{v}} \exp\left(-\frac{E_{\mathsf{g}}}{k_{\mathsf{B}}T}\right)$$